Rubber-like materials derived from biosourced phenolic resins

G. Amaral-Labat[1,2], L.I. Grishechko[1,3], G.F.B. Lenz e Silva[2], B.N. Kuznetsov[3,4], V. Fierro[1], A. Pizzi[5,6] and A. Celzard[1]

[1] Institut Jean Lamour - UMR Université de Lorraine – CNRS n°7198. ENSTIB, 27 rue Philippe Séguin, CS 60036, 88026 Épinal Cedex, France
[2] University of São Paulo, Department of Metallurgical and Materials Engineering PMT-USP, Avenida Mello Moraes, 2463-Cidade Universitária, CEP 05508-030, - São Paulo, SP – Brazil
[3] Institute of Chemistry and Chemical Technology, SB RAS, 50/24, Akademgorodok Street, Krasnoyarsk 660036, Russia
[4] Siberian Federal University, 79, Svobodny Avenue, Krasnoyarsk, 660041, Russia
[5] LERMAB, Université de Lorraine, 27 rue Philippe Séguin, CS 60036, 88026 Épinal cedex, France
[6] Dept. of Physics, King Abdulaziz University, Jeddah, Saudi Arabia

Email: alain.celzard@univ-lorraine.fr

Abstract. The present work describes new gels derived from cheap, abundant and non-toxic wood bark extracts of phenolic nature, behaving like elastomers. Especially, we show that these materials might be used as rubber springs. Such amazing properties were obtained by a quite simple synthesis based on the autocondensation of flavonoid tannins in water at low pH in the presence of a plasticizer. After gelation and drying, the materials presented elastic properties that could be tuned from hard and brittle to quite soft and deformable, depending on the amount of plasticizer in the starting formulation. Not only the materials containing the relevant amount of plasticizer had stress-strain characteristics in quasi-static and cyclic compression similar to most commercial rubber springs, but they presented outstanding fire retardance, surviving 5 min in a flame at 1000°C in air. Neither flame propagation nor drips were noticed during the fire test, and the materials were auto-extinguishable. These excellent features make these materials potential substitutes to usual organic elastomers.

1. Introduction

Natural rubber is a well-known material produced at the level of several million tons every year and used for many centuries, as the first uses were reported in the ancient Aztecs' and Mayans' culture [1]. Despite its quite valuable properties, its limited supply at some periods of the 20th century – or at least the existing gap between production and fast-growing world demand – encouraged the development of synthetic rubbers, despite many of them were technically not as good as natural rubber [2]. Whether natural or not, rubbers are elastomers obtained after a crosslinking step, called vulcanization in this context, and after which the polymer chains have enough mobility to reorganize for redistributing an applied stress. The crosslinks allow that the material recovers its initial shape and dimensions once the

stress is removed. Most elastomers are based on polyenes, mainly as copolymers based on isoprene or butadiene, although polyurethane and polysiloxane also deserve being called "rubbers" [3].

In the present work, rubber-like materials were prepared and characterized from plant-derived polyphenols. Whereas such raw materials are famous for giving hard resins from which adhesives can be obtained mainly for wood products [4], getting soft and elastic solids was unexpected. This could be achieved, however, by using the relevant plasticizer in relevant amounts so that neither the material remained brittle nor the crosslinking was prevented. In the following, the main steps describing the synthesis of these new rubber-like materials are presented, as well as a selection of physical and chemical properties.

2. Materials preparation and characterization

2.1. Materials preparation

The preparation method of rubber-like phenolic materials is described below. It reports how simple the synthesis is, as it only requires 3 very common and cheap compounds and nothing else but a minimalist laboratory equipment: a mixer, an oven, and glass tubes.

2.1.1. Chemicals. One of the originalities of the present work is using condensed (flavonoid) tannin as the base of the elastic resin from which the materials were prepared. Condensed tannin was supplied by the company SilvaChimica (Italy) and was used without purification. It is a natural extract from black wattle trees, sold under the name Fintan OP, and obtained by leaching barks with a warm aqueous solution of sodium bisulphite at 1 wt.%. After spray-drying of the concentrated solution, a light brown powder is obtained which is soluble in water, see figure 1. A typical oligomer constituting about 80% of the tannin extract is also shown in figure 1 [5]. It can be easily crosslinked with aldehydes, such as formaldehyde [5], thereby leading to hard resins. However, this kind of tannin is also prone to autocondensation, provided that the pH is low enough [6].

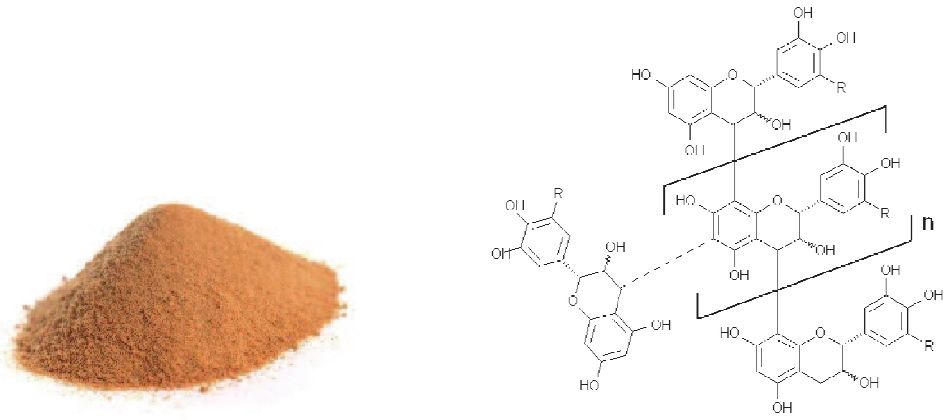

Figure 1. Black wattle bark extract (left) and corresponding oligomer (right), in which *n* typically ranges from 1 to 9.

Low pH was reached by use of para-toluenesulphonic acid (p-TSA), having the advantage of being both a strong and solid acid. This allowed significant changes of pH with negligible dilution. Finally, ethylene-glycol (EG) was used as plasticizer.

2.1.2. Synthesis. Tannin (T) was first dissolved in distilled water (W), and the solution was stirred magnetically until complete homogenization. The stirring was maintained when adding successively para-toluenesulphonic acid (p-TSA) followed by ethylene-glycol (EG). The corresponding formulations are given in table 1, which shows that various ethylene-glycol to water (EG/W) weight

ratios were tested while keeping a constant amount of T and p-TSA. The final, brown solutions were introduced in glass tubes which were hermetically closed afterwards and let for curing in an oven at 85°C for 5 days. The time spent in the oven was enough to produce the gelation of the solutions. Then the glass tubes were broken, the materials were recovered in the form of long cylinders of diameter 1 cm, and left for one full month in air. During this second period, the gels dried and shrank until a constant diameter was reached. Based on the observed dimensional changes, it is assumed that the properties stabilised after this time so that the samples were ready for characterisation. The names of the samples were given according to their EG/W weight ratio, as shown in table 1.

Table 1. Formulations of rubber-like materials and their bulk density.

Samples	EG/W (g/g)	EG/W (wt. %)	T/pTSA (g/g)	(T+pTSA)/total) (wt. %)	Bulk density (g cm^{-3}) ± 5%
TEG(0)	0/15	0	5/0.8	28	1.49
TEG(20)	3/12	20	5/0.8	28	1.43
TEG(33)	5/10	33	5/0.8	28	1.45
TEG(47)	7/8	47	5/0.8	28	1.42
TEG(60)	9/6	60	5/0.8	28	1.46

2.2. Materials characterization

The materials were characterized through a limited number of methods, in order to describe their main characteristics in terms of mechanical properties and fire retardance. As far as rubber-like materials are concerned, many other intrinsic properties might have been investigated as well, and will be in the near future, but the present paper only aimed at presenting such new materials and their principal features.

2.2.1. Bulk density. The materials were cut into cylindrical blocks of carefully measured diameters and heights, typically 8-10 mm and 7-11 mm, respectively. 2 to 5 samples of the same kind were investigated, and the average density was then calculated.

2.2.2. Mechanical tests. Compression tests were carried out as follows in the quasi-static regime, using an Instron 5944 universal testing machine equipped with a 2 kN load cell. First, samples of identical dimensions (typical diameter 8-10 mm and typical height 5-6.5 mm, so as to maintain a constant diameter/height ratio) were compressed with a rate of 2 mm/min until they collapsed completely or broke into pieces. From the corresponding stress-strain curves, elastic modulus and compression strength were determined. The former was estimated from the slope of the initial, linear part of the curve, whereas the latter was assumed to correspond to the upper limit of the elastic regime, i.e., to the point at which a strong change of slope is noticed.

A second set of samples was then used for cyclic compression tests. Unlike the former experiments for which the strain was not limited, the compression was carried out until 10% strain at the same compression speed of 2 mm/min. 50 successive compression-decompression tests were performed, applying a recovery time of 1 min between each cycle.

2.2.3. Fire tests. One sample was put directly into the flame of a propane burner fed by an excess of air, more exactly in the zone wherein the temperature is the highest, about 1000°C, i.e., just at the tip of the blue cone. The sample weight was measured before and after 5 min spent in the flame.

3. Results and discussion

3.1. Materials aspect and general features

The materials were all black and shiny, irrespective to their initial formulation. Figure 2 illustrates the case of TEG(33) sample, for which the elastic character is easy to appreciate as soon as the gel is gently pressed between the fingers. The method by which the materials were prepared suggests that they can be obtained without limit of size and in any shape, the latter only depending on the characteristics of the mold.

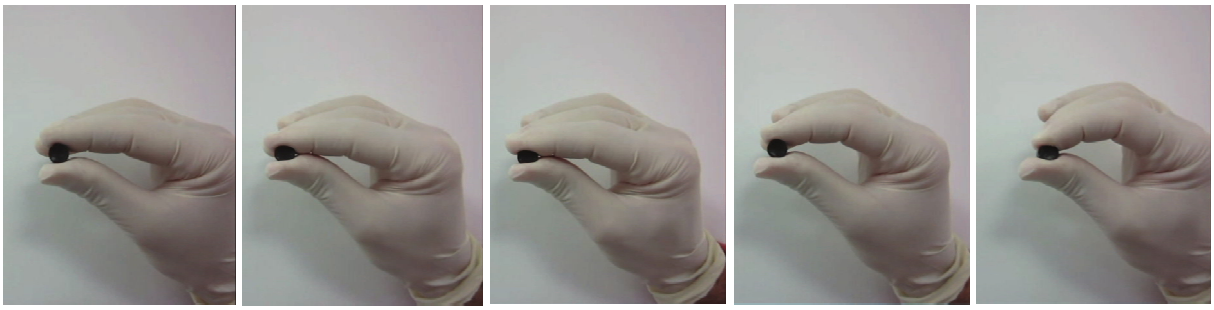

Figure 2. Sequence (from left to right) of compression-release stresses applied to TEG(33) sample between fingers, showing the ease by which it can be deformed while recovering immediately.

The density values reported in table 1, 1.45 g cm^{-3} ± 3% on average, were very close to each other. This suggests that, at fixed content of solid phase, water and ethylene glycol were both equally incorporated and took part to the samples bulk, and that EG replaced water without producing any noticeable shrinkage or swelling.

3.2. Mechanical properties

As already suggested by figure 2, all materials except TEG(0) were very soft and elastic. This is shown in figure 3, where the compressive stress was plotted as a function of strain. A clear trend can be observed from TEG(0) to TEG(60), corresponding to an increasing amount of plasticizer in the formulation. As TEG(0) did not contain ethylene glycol at all, it behaved as most other tannin-based resins so far, i.e., presented a hard and brittle behaviour [7]. This is evidenced by the steep, first part of the curve, corresponding to a much higher modulus than for the other materials, followed by a brittle failure. In contrast, the other materials became softer and softer when the amount of plasticizer increased. Thus, the general shape of the curves presented by TEG(20) to TEG(47) are typical of what is known for commercial rubber springs, and with similar values of both stress and strain [8]. It is then expected that these materials can be used for the same applications. TEG(60) is, however, probably too weak, as suggested by its rather flat curve shown in figure 3.

The aforementioned trends also apply to the compressive strength, defined as the stress at the change of slope of the curves, i.e., at around 10-15% strain. The higher was the EG content, the lower was the strength. The corresponding values of modulus and strength are gathered in table 2. TEG(60) was logically the softest material, and corresponded to the limit of this range of materials. Formulations presenting higher amounts of ethylene glycol indeed did not gel, from where the range of compositions formerly presented in table 1.

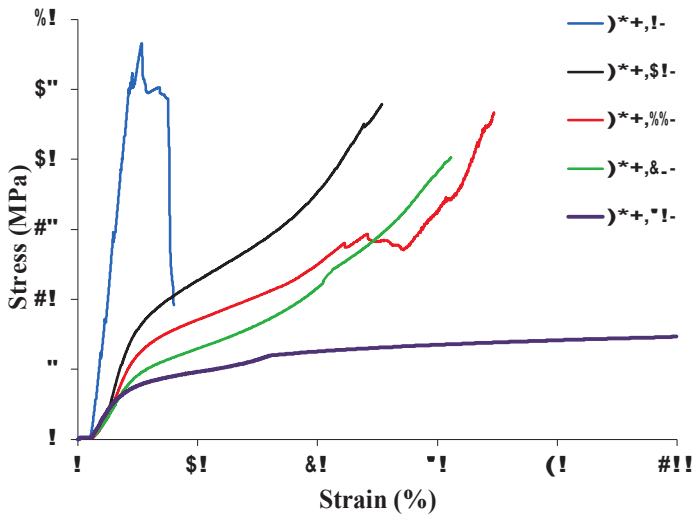

Figure 3. Stress-strain characteristics of rubber-like materials submitted to compression at a loading rate of 2 mm/min and without limitation of strain.

Table 2. Elastic moduli and compressive strengths derived from figure 3.

Samples	Elastic modulus (MPa)	Compressive strength (MPa)
TEG(0)	381	25.0
TEG(20)	141	10.7
TEG(33)	101	6.4
TEG(47)	68	5.2
TEG(60)	72	4.1

TEG(33) sample before and after compression test is shown in figure 4. Even after having been compressed at a strain as high as 40%, it completely recovered its initial height, although around 10 min were required for this. Such severe deformation, far beyond what is requested for rubber springs (usually limited from 15% to 25% strain [9]), produced an irreversible change of diameter. Interestingly, the latter was lower after than before the test, suggesting a negative Poisson ratio.

Figure 4. TEG(33) sample before (left) and 10 min after (right) compression tests up to 40% strain at 2 mm/min.

However, lower strains such as those usually encountered in rubber spring applications did not produce any dimensional change, and the same sample recovered completely again after many stresses applied up to 10% strain. Figure 5 thus shows a series of 50 successive compression-decompression curves for the same TEG(33) material. As can be seen, the cycles became nearly impossible to separate beyond cycle #30.

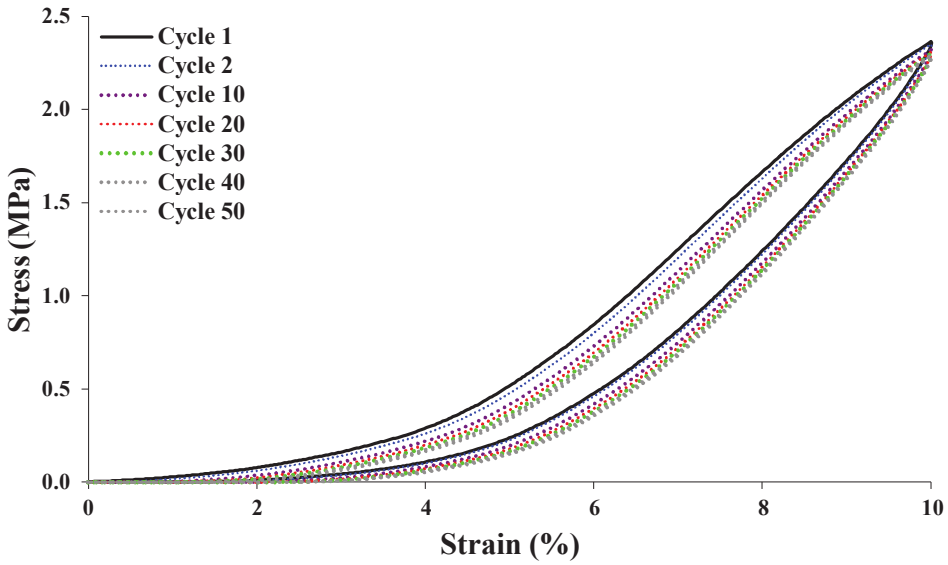

Figure 5. Successive compression-release cycles for TEG(33) up to 10% strain at 2 mm/min, with 1-min recovery between each cycle.

From the hysteresis loops presented in figure 5, the energy loss coefficient was calculated as the area below the loading curve minus the area below the unloading curve [10]. This parameter corresponds to the ease with which a material can recover and hence retain its elastic properties. The values given in figure 6 indicate that the energy that can be dissipated is quite high, as it should be expected for a rubber spring.

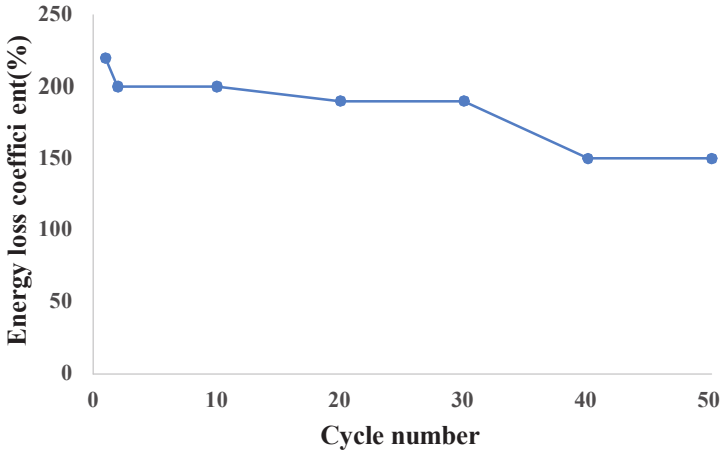

Figure 6. Energy loss coefficient derived from figure 5.

3.3. Fire retardance

The fire retardance of these materials was found to be outstanding. Such feature is already known for phenolic resins in general, which are indeed used as foundry sand resins in the metal casting industry, or as classical matrix in ablative composites or friction materials [11]. When heated, these materials indeed tend to decompose into glassy carbon whereas a very low amount of poorly flammable gas is released. During such degradation process, a significant amount of heat is absorbed, and almost no flame is produced. Whereas this phenomenon had to be expected because of the highly aromatic character of the crosslinked phenolic resin [12], observing it with rubber-like materials still is amazing.

Figure 7 thus presents TEG(33) sample submitted to a burner at 1000°C. No flame appeared at the surface of the sample all along the test, but only a little smoke was emitted at the beginning (see the orange colour after 1 min in figure 7). When taken out of the burner, the red-glowing sample auto-extinguished immediately. After 5 min, the weight loss was around 65% and, as expected, the material completely lost its elastic character and became very hard. However, it survived, as shown in the last photo of figure 7. In so severe conditions, any other usual organic elastomer would have burnt completely with flames and, in some cases, with release of faming drips.

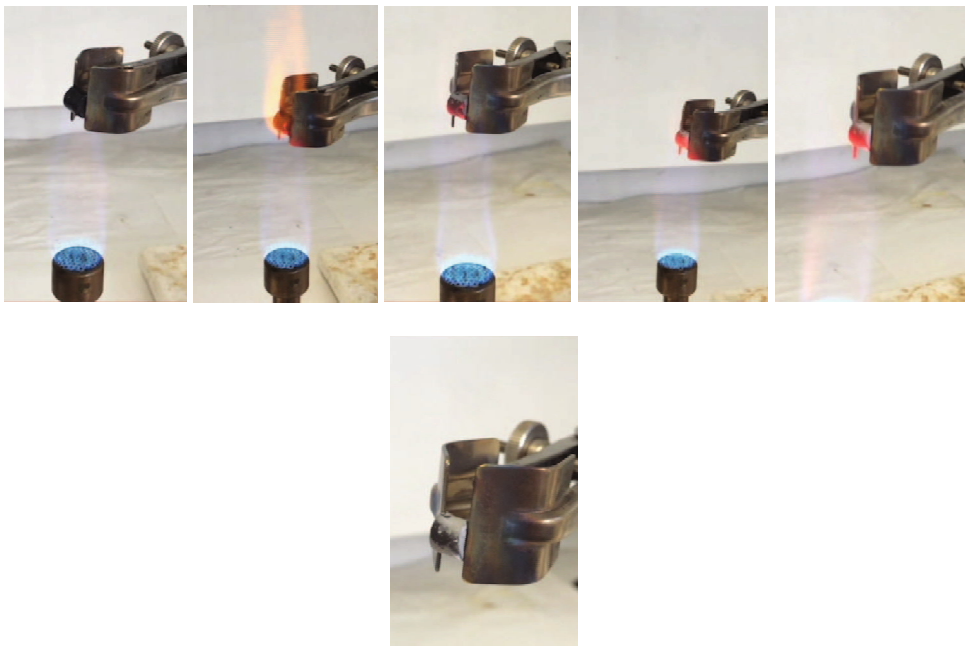

Figure 7. Top raw: view of TEG(33) sample submitted to the flame of a propane burner at 1000°C at times t = 0, 1 min, 2 min, 3.5 min, and 5 min (from left to right). Bottom: view of the same sample at 5 min just after removing the flame.

4. Conclusion

The first rubber-like materials based on a natural source of phenolic resin, flavonoid tannin, were reported. They were prepared from an ultra-simple mixing of commercial wattle bark extract in water with ethylene glycol and para-toluenesulphonic acid, subsequently let for curing for 5 days at 85°C and dried in room conditions for one month.

These new materials proved to behave as true elastomers in compression, whereas their chemical structure had nothing to do with classical vulcanizates. In the present case, the oligomers crosslinked by autocondensation, as no crosslinking agent such as formaldehyde was requested. The presence of ethylene glycol (EG), acting as internal plasticizer, allowed observing various mechanical behaviors,

from hard and brittle in the complete absence of EG to ultra-soft with the highest possible amount of EG. Therefore, a range of materials could be obtained just by playing with the concentration of EG in the formulation, all the other parameters being kept constant. The material with the medium content of EG was found to be able to dissipate a significant amount of energy when used as rubber spring, and its stress-strain characteristics were indeed quite similar to those of commercial elastomers used for the same application. Moreover, the reversibility of the compression-release curves was complete after 30 cycles up to 10% strain.

Besides being new biosourced rubber-like materials, the latter also presented an outstanding fire retardance related to their phenolic nature. The sample with the medium content of EG lost it elastic properties but survived after having been submitted to a flame at 1000°C during 5 min. No ignition could be observed, and the material was auto-extinguishable.

Such advantageous properties definitely demonstrate the interest for these new materials for springs, and further studying their properties is worth doing in the near future.

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